Mineralogy and microporous structure of rocks from a natural CO_2 reservoir

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1. Introduction and Aims

- Different experimental approaches have been combined to reconstruct the mineral association and microporous structure of rocks from a natural CO_2 reservoir.
- The fluid reservoir (**Caprese Reservoir**), was discovered while drilling **PSS1** (Pieve Santo Stefano 1) wellbore in San Cassiano Basin (Eastern Tuscany, Central Italy; Fig.1a; [1,2]) and consists (Fig.1b) of sedimentary rocks (Burano Fm.) interbedded with altered volcanic rocks, its depth being about 3,300 m with respect to the land surface. At 3,700 m depth fluid pressure and temperature are 700 bar and 120 °C respectively, with a density for the supercritical CO_2–rich fluid of 840 Kg·m^{-3}.
- The study was conducted on the volcanic rocks altered by CO_2 from the PSS1 wellbore drillcores and on some volcanic rocks unaffected by the presence of CO_2. Lastly, rocks from the Burano Formation, unavailable from PSS1, have been sampled on outcrop.
- Focus is on rocks samples corresponding to the depth 3,864-3,871 m with respect to PSS1 log, which have been investigated with **SEM-EDS and XRD** for mineralogical characterization. Moreover, Small Angle Neutron Scattering (**SANS**) experiments [3] at LLB (Saclay, France) served for microporous structure investigation of PSS1 rocks, and other volcanic rocks from Eastern Alps (IG1) and the Albani Hills (IG2 and IG3) unaffected by CO_2, as well as Burano Formation rocks from outcrop.

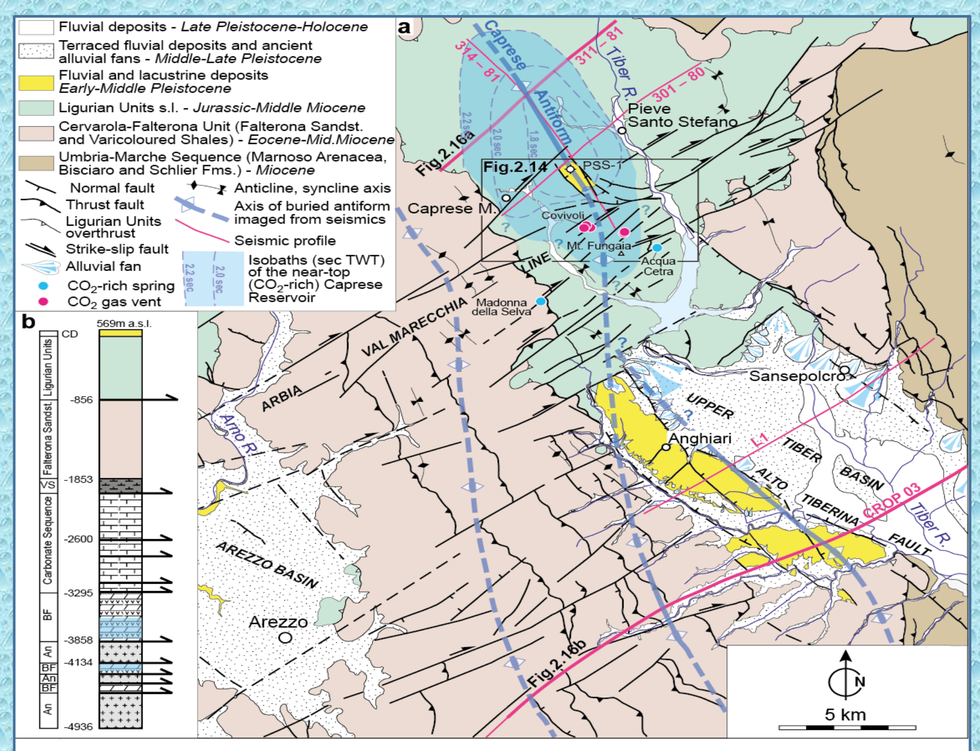

Figure 1 (a) Schematic geological-structural map of the area around the 'PSS1' wellbore [1]. (b) Schematic reconstruction of stratigraphic column from well log (modified after [2]). Cd = San Cassiano Pleistocene Continental Deposits, VS = Varicoloured Shale, An = Andesite, BF = Burano Formation. The tectonics discontinuities are represented with bold black arrows.

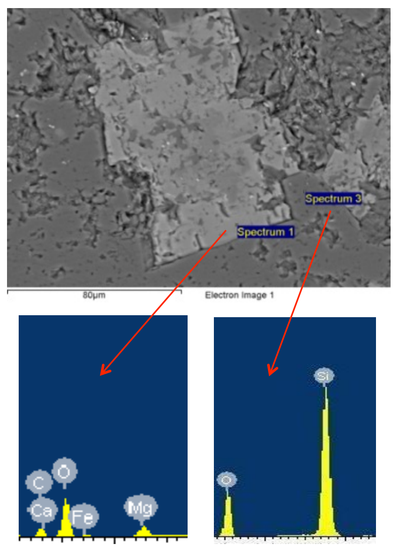

Figure 2. SEM-EDS back-scattered (BS) photo (top) and spectra of ankerite (on the left, lighter minerals on BS photo) and quartz (on the right, darker minerals in the BS photo).

Rocks not affected by CO_2

Sample ID	D_s
Burano	2.41 ± 0.09
IG1	2.36 ± 0.05
IG2	2.33 ± 0.04
IG3	2.52 ± 0.04

Rocks affected by CO_2

Sample ID	D_s
3,864	2.11 ± 0.03
3,866	2.13 ± 0.06
3,867	2.45 ± 0.05
3,868	2.34 ± 0.05
3,870	2.76 ± 0.05
3,871	2.63 ± 0.05

Table 1. Surface fractal dimension D_s from a generalized Porod law applied to some of the PAXE data (λ = 7.8 Å).

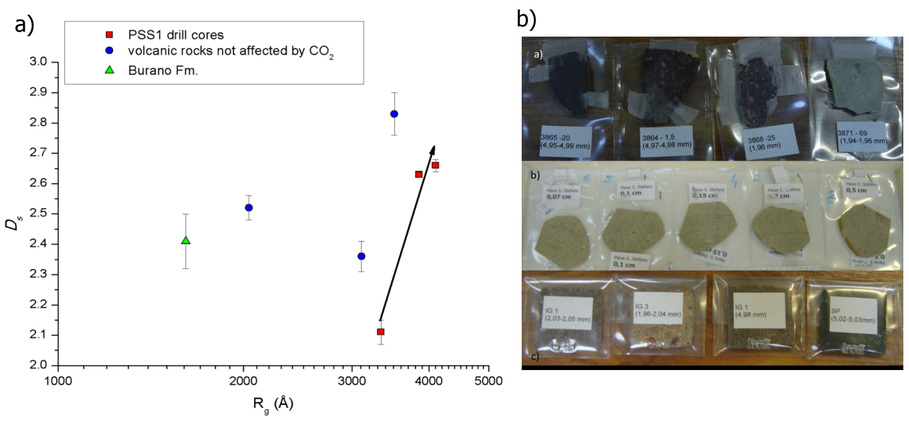

Figure 3. a) Fractal surface dimension D_s vs. radius of gyration (R_g in logarithmic scale) in the samples of volcanic rocks from PSS1 and from those of unaltered by CO_2 and of Burano formation. Experimental error on D_s is shown in the figure as bars, error on R_g is within the symbols; b) samples of rock analysed with SANS.

4. Concluding Remarks

•Results about the surface fractal properties (from SANS experiments) indicate a dispersion of the fractal dimensions values in the reservoir rocks significantly larger than in the values found in rocks not affected by CO_2 presence.

•This trend is confirmed by chemical and mineralogical analyses, which highlight extremely inhomogeneous compositions.

•Chemical alteration promoted by CO_2-rich fluids is inhomogeneous, affecting the reservoir rocks along preferential paths (i.e. joints and fractures) interested by intense fluid circulation.

2. Mineral forming rocks

•According to E.N.I. PSS1 log, wellbore rocks are of volcanic origin. Nevertheless, the presence of the CO_2–rich fluid has completely obliterated the original mineralogical assemblage. The latter is indeed mainly consisting of **Na-K illite** (62-85 wt. %) and **quartz** (12.0 to 33.7 wt. %). Carbonates minerals, i.e. **ankerite** (up to 12.5 wt. %) and **calcite** (up to 3.63 wt. %), represent an important part of the composition. All these minerals are typically characterized by rather small grain size (from 100 to less than 10 µm; Fig.2), precipitated from an aqueous fluid circulating in the reservoir together with the CO_2-rich gas phase [1].

•The volcanic rocks, studied for comparison and unaffected by CO_2, are mainly composed of quartz, feldspars and mica (muscovite and biotite). Finally, rocks of Burano Fm. consist of dolomite and gypsum.

3. Microporosity Characterization by Small Angle Neutron Scattering

3.1 Pore size

The average pore size has been evaluated on samples with 2 mm thickness, looking at the lower wavevector Q-range investigated with TPA spectromter (λ = 12 Å) and applying a Guinier-like model:

$$\ln(I) = AQ^2 + B$$

where I is the intensity as a function of Q. The radius of the assumed spherical pores, related to the A coefficient, comes out to be roughly between 3300 and 4100 Å for the volcanic rocks samples of the wellbore, while is significantly smaller, i.e. approximately between 2000 and 3100 Å, for the possible analogues of the same volcanic rocks coming from outcrops and therefore believed not affected by CO_2.

3.2 Pore-rock interface fractal dimensions

If the data are modelled with a generalized Porod behaviour, i.e. with a power law:

$$I(Q) = I_1 Q^{-x} + B$$

from the exponent x the fractal dimension D_s for surface ($3<x<4$, with $D_s=6-x$) or D_m for mass/volume ($2<x<3$, with $D_m=x$) can be derived [4].
We have applied this approach to the PAXE data (λ = 7.8 Å) in the 1.13-5.58·10^{-2} Å^{-1} range. The values of D_s for the CO_2 altered volcanic rocks lay in a wide range (Tab .1), showing differences of more than 30% from sample to sample, although they pertain to a contiguous drill core that is less than 10 meters long.

In contrast, the D_s values relative to the "analogue" volcanic rocks, unaffected by CO_2 alteration, are confined between 2.33±0.04 and 2.52±0.04, although these rocks come from different geological contexts. In the PSS1 wellbore rocks, it is worth mentioning that there is a direct correlation between the radius of gyration and the D_s, i.e. the higher are the values of surface fractal dimension the larger are pores sizes (Fig. 3a). Similar features were documented in metamorphic rocks affected by fluid circulation [5].

References

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